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THE MILLIMETER- AND SUBMILLIMETER-WAVE SPECTRUM OF METHYL FORMATE ($HCOOCH_3$)

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ABSTRACT

Methyl formate ($HCOOCH_3$), a threefold internal rotor, is a well-known interstellar molecule located in hot cores of giant molecular clouds. Over a decade ago, we published separate analyses of the rotational-torsional spectra of methyl formate in its A and E ground torsional substates. The analysis of the A substate was undertaken with a standard asymmetric top Hamiltonian, while that of the E substate was undertaken with a principal axis method (PAM), which was less than entirely satisfactory. In the interim, we have measured many new lines of the rotational-torsional spectrum of both the ground A and E torsional substates of this species through the rotational quantum number $J = 50$ using two spectrometers: our standard klystron-based system and a new fast scan spectrometer (FASSST). The newly measured lines have been combined with previous data to form a data set consisting of over 2000 lines that has been fitted to the accuracy of our experiments using a modification of the internal axis method (IAM) we have previously applied to methanol. The spectral constants obtained from the fit have allowed us to predict the frequencies of many additional lines up to 700 GHz in frequency and up to $J = 50$ in rotational quantum number.

Subject headings: ISM: molecules — line: identification — methods: laboratory — molecular data — radio lines: ISM — submillimeter

1. INTRODUCTION

Methyl formate ($HCOOCH_3$) is a well-known interstellar molecule that is found in hot cores of giant molecular clouds such as Orion KL (Schilke et al. 1997; Blake et al. 1987) and Sgr B2(N) (Snyder, Kuan, & Miao 1994; Miao et al. 1995). Hot cores are dense, warm regions in the vicinity of sites of high-mass star formation. Although the details of its formation are not known precisely, it is thought that methyl formate derives from the precursor molecules methanol (CH_3OH) and formaldehye (H_2CO), enhanced abundances of which come from the evaporation of mantles of dust particles as the temperature rises (Brown, Charnley, & Millar 1988; Millar, Herbst, & Charnley 1991; Charnley, Tielens, & Millar 1992). Once in the gas phase, methanol can be partially protonated to form the molecular ion $CH_3OH_2^+$; this ion may then react with formaldehyde to form protonated methyl formate:

$$CH_3OH_2^+ + H_2CO \rightarrow H_2COOCH_3^+ + H_2 \, . \qquad (1)$$

Protonated methyl formate then leads directly to methyl formate via dissociative recombination with electrons (Millar et al. 1991; Caselli, Hasegawa, & Herbst 1993).

The relatively large abundance of methyl formate in hot core sources coupled with its dense rotational-torsional spectrum has led to the identification of a large number of interstellar spectral lines, prompting some to label methyl formate as an "interstellar weed." Much of the previous analysis of interstellar methyl formate was based on several millimeter-wave laboratory studies we carried out more than a decade ago (Plummer et al. 1984, 1986; Plummer, Herbst, & De Lucia 1987). Still earlier work at lower frequencies had been undertaken by Curl (1959), Bauder (1979), and DeMaison et al. (1983).

The rotational spectrum of methyl formate is complicated by the large amplitude motion of the protons of the methyl (CH_3) group, which is known as internal rotation, or torsion. This motion leads to torsional energy levels, characterized by the quantum number $v_t = 0, 1, 2, \ldots$, and separated by 50–100 cm^{-1}. Each torsional level is in turn split into two substates, characterized by the symmetry labels A and E (Gordy & Cook 1984; Lin & Swalen 1959). In addition, the torsional and end-over-end rotational motions are coupled such that the rotational energy levels and selection rules within torsional substates differ from standard asymmetric top patterns, especially in E substates. The strength of this coupling is highly dependent on the particular molecule being studied; in methyl formate it is far weaker than in methanol, another subject of study in this laboratory (see, e.g., Anderson, Herbst, & De Lucia 1992). Rotational-torsional transitions involving different torsional states ($\Delta v_t \neq 0$; A–A, E–E) typically produce spectra in the far-infrared region, whereas transitions within one torsional substate produce spectra in the microwave, millimeter-wave and submillimeter-wave regions. To the best of our knowledge, there have been no successful high-resolution studies of far-infrared transitions of methyl formate, nor have there been any studies of transitions within excited torsional states ($v_t > 0$).

In our first study (Plummer et al. 1984), we measured over 200 rotational-torsional spectral lines of methyl formate in its ground ($v_t = 0$) symmetric (A) torsional substate in the frequency range 140–550 GHz. Since the coupling with torsional motion is weak for this substate, we were

able to analyze our transitions plus previously measured ones with a standard asymmetric top Hamiltonian (Gordy & Cook 1984). The analysis allowed accurate prediction of a large number of lines below 500 GHz in frequency and with rotational quantum number $J \leq 50$. Our next study, of the ground E torsional substate, was not as successful, although we measured and assigned over 250 transitions. In this substate, torsional coupling must be considered, and we utilized a perturbative treatment known as the principal axis method (PAM; Herschbach 1959; Gordy & Cook 1984). With this approach, even when taken to high order, we were not able to fit our measured lines and those of previous investigators to the accuracy of the experiments. Moreover, accurate predictions were limited to transitions below 300 GHz in frequency and rotational quantum numbers $J \leq 30$. Finally, we ran into difficulty deciding on the correct selection rules and intensities for an assortment of transitions (Plummer et al. 1987). Nevertheless, our treatment was instrumental in assigning many interstellar lines in Orion (Blake et al. 1986).

In the years following our work on methyl formate, we developed a far more powerful technique of spectral analysis for internal rotor molecules and utilized it to analyze methanol (Herbst et al. 1984; De Lucia et al. 1989; Anderson et al. 1992; Belov, Winnewisser, & Herbst 1995) and other species such as methyl mercaptan (Bettens et al. 1999). This technique, known imprecisely as the internal axis method (IAM; Lin & Swalen 1959; Lees & Baker 1968; Kochler & Dennison 1940) and more precisely as the ρ-axis method (Xu & Lovas 1997), is not perturbative in origin and removes much of the coupling between rotational and torsional motions by a series of axis rotations. Use of our IAM approach does require the diagonalization of large matrices connecting rotational-torsional energy levels. With the vast increases in computer power that have become available in the last decade, it is now straightforward and desirable to apply the technique even to molecules in which internal rotor effects are not dramatic. We have previously used it in a study of the symmetric deuterated isotopomer of methyl formate—$DCOOCH_3$ (Oesterling et al. 1995). In this paper, we report a new study of methyl formate in which large numbers of newly measured rotational-torsional transitions in the ground A and E torsional substates have been combined with previous data into one large global data set of 2482 lines consisting of transitions involving $J \leq 50$. The data set has been analyzed successfully via the IAM approach. Our analysis allows us to predict accurately the frequencies of over 12,000 additional transitions through 700 GHz in frequency. Extensions of the upper frequency limit, if required in the future, will be relatively straightforward except for possible difficulties in the intensity calculations.

2. EXPERIMENT AND SPECTRAL ANALYSIS

Prior to our earlier work, the measured rotational-torsional spectrum of methyl formate consisted of about 350 lines through 240 GHz in frequency. Of these transitions, Curl (1959) measured 29 lines at frequencies in the range 8–30 GHz, Bauder (1979) measured 200 lines at frequencies through 58 GHz, and DeMaison et al. (1983) measured more than 100 lines, mainly in the 220–240 GHz region. In our earlier measurements, over 450 new lines were fitted and assigned, leading to a good knowledge of the spectrum for the $v_t = 0$ A substate spectrum through 500 GHz and $J \leq 50$, and an adequate knowledge of the spectrum for the $v_t = 0$ E substate through 300 GHz and $J \leq 30$. We have now "supplemented" these data with many measurements through 608 GHz in frequency involving rotational transitions with $J \leq 50$ in the ground torsional substates. The new lines have been measured with two types of apparatus—a standard klystron-based spectrometer (Helminger, Messer, & De Lucia 1983) and a new type of fast scan submillimeter system which we have dubbed FASSST, an acronym standing for "fast scan submillimeter spectroscopic technique" (Petkie et al. 1997). In this latter system, the submillimeter-wave radiation is provided by a voltage tunable backward wave oscillator (BWO), which is scanned rapidly through a large frequency range. The experimental accuracy of the lines measured with both techniques is typically 100 kHz. The total number of lines in our inclusive data set now consists of 1190 for $HCOOCH_3$-A and 1292 for $HCOOCH_3$-E, of which $\approx$1650 have been newly measured. All of these lines arise from transitions in the ground ($v_t = 0$) torsional substates; we have still not been able to identify and assign rotational transitions arising from excited torsional states.

The spectral lines have been fitted by use of an IAM program that is modified in two ways from that used for methanol (Anderson et al. 1992; De Lucia et al. 1989; Herbst et al. 1984). First, whereas for methanol the A and E analyses were performed separately, for methyl formate we analyzed the two sets of transitions in one global fitting procedure. Second, since methyl formate is more of an asymmetric top and less of an internal rotor than methanol, we replaced many of the spectral constants defined in Anderson et al. (1992) with more standard but high-order centrifugal distortion constants (Gordy & Cook 1984). An unweighted root mean square deviation of 145 kHz, which is essentially experimental accuracy, was obtained for the global data set by varying 52 rotational-torsional parameters. For those lines arising from transitions in the $v_t = 0$ E substate, this fit is far superior to that achieved by our previous approach.

The fitted spectral transitions for the A and E substates are listed in Tables 1 and 2, respectively (only the first 20 rows of each table are found in the paper edition; for the complete versions, see the electronic edition). In addition to the frequencies, the tables contain quantum assignments (single primes stand for upper levels while double primes stand for lower levels), residuals (observed − calculated frequencies), upper and lower state energies (cm^{-1}), and intensities expressed as the square of the relevant component of the dipole moment (Debye) multiplied by the S value (Townes & Schawlow 1975). The measured values of the dipole components are $\mu_a = 1.63$ Debye, $\mu_b = 0.68$ Debye (Bauder 1979); these are expressed in the principal axis system. Rotation into the internal axis system used in our analysis leads to very different components ($\mu_a \approx -1.2$ Debye, $\mu_b \approx 1.3$ Debye) since the a and b axes are rotated by an angle of almost 30° to go from one system to the other (Oesterling et al. 1995). We found the dipole components in the internal axis system by a process consisting of an actual geometrical analysis plus a constraint that the computed intensities be the same using both the internal and principal axes. The intensities, computed via our IAM approach, are normally accurate to $\approx$10%–20%. Comparison of the frequencies in Tables 1 and 2 shows that, unlike the case of methanol, the differences between transitions with the same

TABLE 1

ASSIGNED AND FITTED TRANSITION FREQUENCIES OF METHYL FORMATE IN THE GROUND *A* TORSIONAL SUBSTATE

J'	K_a'	K_c'	J''	K_a''	K_c''	Frequency (MHz)	Residual (MHz)	E_u (cm^{-1})	E_l (cm^{-1})	$\mu^2 S$
30	8	22	30	8	23	8844.515	−0.013	222.3	222.0	8.4
6	4	3	7	3	4	8910.032	0.043	16.0	15.7	0.2
39	10	29	39	10	30	10413.575	0.079	369.6	369.2	9.4
6	2	4	5	3	3	10718.577	−0.064	10.7	10.3	0.2
14	4	10	14	4	11	11216.260	0.017	51.1	50.7	4.8
2	0	2	1	1	1	11227.499	−0.008	1.2	0.8	0.3
35	9	26	35	9	27	12029.804	0.045	298.7	298.3	8.6
1	0	1	0	0	0	12219.209	0.002	0.4	0.0	2.7
31	8	23	31	8	24	13652.665	0.005	235.4	235.0	7.8
9	3	7	8	4	4	14012.303	−0.081	22.6	22.2	0.4
1	1	0	1	0	1	14681.231	0.010	0.9	0.4	0.7
4	1	3	3	2	2	14903.145	−0.031	4.8	4.3	0.2
40	10	30	40	10	31	15677.131	0.117	386.5	386.0	8.7
2	1	1	2	0	2	16431.284	0.010	1.8	1.2	1.0
36	9	27	36	9	28	18040.836	0.081	314.0	313.4	7.9
2	0	2	1	0	1	24298.476	−0.005	1.2	0.4	5.4
3	0	3	2	1	2	24504.165	−0.011	2.4	1.6	0.6
12	3	9	12	3	10	24649.431	0.002	37.0	36.1	2.9
1	1	1	0	0	0	25290.161	−0.021	0.8	0.0	0.4
20	5	15	20	5	16	25530.745	0.035	99.2	98.4	4.5

NOTE.—Table 1 is published in its entirety in the electronic edition of The Astrophysical Journal. A portion is shown here for guidance regarding its form and content.

quantum numbers in the *A* and *E* torsional substates are quite small, typically under 100 MHz.

The rotational quantum numbers used are asymmetric top entities (J, K_a, K_c), where K_a and K_c are pseudo-quantum numbers referring to the projection of the angular momentum along the *a* and *c* principal axes. Since methyl formate is an internal rotor, the use of the asymmetric top labels (which is essentially an ordering procedure since only J is an actual quantum number) can be somewhat arbitrary and lead to transitions that do not obey standard asymmetric top selection rules (Plummer et al. 1987). In particular, in addition to the standard *a*-type ($\Delta K_a = 0$, $\Delta K_c = \pm 1$) and *b*-type ($\Delta K_a = \pm 1$, $\Delta K_c = \pm 1, \pm 3$) transitions expected for a molecule with dipole components along these axes (Townes & Schawlow 1975), we find transitions in the *E* substate that can be characterized as *c*-type ($\Delta K_a = \pm 1$,

TABLE 2

ASSIGNED AND FITTED TRANSITION FREQUENCIES OF METHYL FORMATE IN THE GROUND *E* TORSIONAL SUBSTATE

J'	K_a'	K_c'	J''	K_a''	K_c''	Frequency (MHz)	Residual (MHz)	E_u (cm^{-1})	E_l (cm^{-1})	$\mu^2 S$
1	1	0	1	1	1	1610.910	0.010	0.9	0.9	4.0
6	2	4	6	2	5	8570.750	0.054	10.7	10.4	3.0
30	8	22	30	8	23	8828.415	−0.063	222.3	222.0	8.4
3	1	2	3	1	3	9647.160	0.020	3.1	2.8	1.6
26	7	19	26	7	20	9819.330	−0.015	168.2	167.9	7.6
39	10	29	39	10	30	10397.132	−0.047	369.6	369.2	9.4
10	3	7	10	3	8	10466.110	0.080	27.1	26.7	3.9
2	0	2	1	1	1	11230.660	0.054	1.2	0.9	0.3
35	9	26	35	9	27	12008.790	−0.060	298.7	298.3	8.6
1	0	1	0	0	0	12218.160	0.026	0.4	0.0	2.7
31	8	23	31	8	24	13628.716	−0.067	235.4	235.0	7.8
7	2	5	7	2	6	14267.300	0.072	13.7	13.2	2.4
1	1	0	1	0	1	14676.760	−0.025	0.9	0.4	0.7
4	1	3	3	2	2	14915.870	0.128	4.8	4.3	0.2
27	7	20	27	7	21	15154.794	−0.034	179.6	179.1	6.9
40	10	30	40	10	31	15651.956	−0.027	386.5	386.0	8.7
4	1	3	4	1	4	16037.310	0.034	4.8	4.3	1.2
2	1	1	2	0	2	16425.070	−0.020	1.8	1.2	1.0
23	6	17	23	6	18	16443.766	0.033	131.4	130.8	6.0
11	3	8	11	3	9	16618.310	0.112	31.8	31.3	3.3

NOTE.—Table 2 is published in its entirety in the electronic edition of The Astrophysical Journal. A portion is shown here for guidance regarding its form and content.

TABLE 3

SPECTROSCOPIC PARAMETERS FOR METHYL FORMATE

Parameter[a]	Value[b]	Uncertainty[b]
A	0.1752236993E+05	0.12E+01
B	0.9323547665E+04	0.11E+01
C	0.5312699963E+04	0.46E+00
D_{ab}	−0.5009721954E+04	0.79E+00
F (cm^{-1}).....	0.5608613000E+01	(fixed)
ρ (unitless).....	0.8375907040E−01	0.23E−04
V_3 (cm^{-1}).....	0.3987634199E+03	0.32E−01
F_v	−0.1318662518E+03	0.22E+01
L_v	0.7583072680E+00	0.14E−01
D_{JK}	−0.8029344793E+00	0.31E−02
D_J	0.1047777577E+00	0.61E−03
D_K	0.8253670094E+00	0.31E−02
k_5	0.6308119089E+03	0.40E+01
δ_J	0.5404345920E−01	0.23E−03
δ_K	−0.9073699089E−01	0.35E−03
c_2	−0.8016027719E+02	0.16E+01
H_J	0.1028798746E−05	0.16E−06
H_{JK}	0.1450838917E−04	0.93E−06
H_{KJ}	−0.1554547381E−03	0.12E−05
H_K	0.1696647849E−03	0.11E−05
h_J	0.1162593561E−05	0.68E−07
h_{JK}	0.7256610083E−05	0.11E−06
h_K	−0.1432041219E−04	0.91E−07
f_v	−0.2280381571E−01	0.23E−02
d_{ab}	−0.1497959141E+03	0.11E+01
L_J	−0.3797624878E−09	0.14E−10
L_{JJK}	0.2327232005E−08	0.10E−09
L_{JK}	−0.1481324450E−07	0.35E−09
L_{JKK}	0.4707900223E−07	0.54E−09
L_K	−0.3858324886E−07	0.37E−09
l_J	−0.1702309114E−09	0.66E−11
l_{JK}	0.1595945747E−09	0.22E−10
l_{KJ}	−0.2259308405E−08	0.46E−10
l_K	0.2369769130E−08	0.49E−10
P_J	0.2137936968E−13	0.92E−15
P_{JK}	−0.1030355120E−11	0.52E−13
P_{KJ}	0.6056631399E−11	0.19E−12
P_{JKK}	−0.1291236753E−10	0.24E−12
P_K	0.8676891929E−11	0.14E−12
p_J	0.5029531983E−14	0.45E−15
p_{JJK}	0.7873231567E−13	0.30E−14
p_{JK}	−0.7728036256E−13	0.90E−14
p_K	0.3164400594E−12	0.45E−13
D_{ab2}[c]	0.5604679840E−01	0.30E−03
ϕ_v	−0.4606183561E−01	0.82E−02
f_k	−0.1303296221E+00	0.50E−02
l_v	0.4815816965E−04	0.70E−05
c_6	−0.3908402516E−02	0.97E−03
H_{J1}[d]	0.2144776503E−04	0.65E−06
H_{JK1}	−0.4429071167E−04	0.28E−05
h_{J1}	0.1416672609E−04	0.56E−06
H_{JK3}	−0.2197510264E−06	0.46E−08
σ (kHz)[e]	145.4	

[a] Parameters, defined in Anderson et al. 1992 unless noted, are listed to 10 significant figures so as to reproduce the predicted spectral data.

[b] Units of megahertz unless otherwise noted. Uncertainties are 1 σ values.

[c] Parameters D_{abJ} are centrifugal distortion constants for D_{ab} to order J

[d] Parameters $H_{..1}$ and $h_{..1}$ are torsional-rotational constants multiplying products of standard sixth-order centrifugal distortion rotational expressions and assorted torsional expressions as defined in Anderson et al. 1992. The nomenclature is new.

[e] Unweighted root−mean−square deviation of the fit to the experimental frequencies (kilohertz).

$\Delta K_c = 0, \pm 2$) and x-type ($\Delta K_a = 0$, $\Delta K_c = 0, \pm 2$). The c-type transitions are especially important for R-branch ($\Delta J = 1$) transitions with high values of K_a and Q-branch ($\Delta J = 0$) transitions at intermediate values of K_a where they replace the b-type transitions. For high values of J, the levels characterized by low successive values of K_a and the same value of K_c are essentially degenerate in both the A and E torsional substates. This degeneracy leads occasionally to some inconsistency as to the proper apportioning of intensities between the degenerate a-type and b-type transitions involving these quantum numbers in our numerical calculations. The total intensity, which should reside mainly in the a-type transitions, is unaffected. Since these pairs of levels are in the oblate symmetric top limit, the approximate ratio of intensities between the a-type and b-type transitions, neglecting weak internal rotor effects, can be obtained from a table of symmetric top intensities to be 5.7 (Townes & Schawlow 1975, see Table 4.4).

The spectroscopic constants determined by the fit are listed in Table 3. It is necessary to fix one rotational parameter—F—at the value obtained previously (Plummer et al. 1986). The determined parameters include standard rotational constants, centrifugal distortion constants, torsional constants, and so-called interaction constants, which pertain to terms in which both rotational and torsional operators appear. The constants are defined in Table 1 of Anderson et al. (1992) except for a few which are defined in footnotes with Table 3 in this paper. Note that the rotational constants cannot be compared with our previous values obtained using principal axes since the a and b principal axes differ by around 30° from those of the internal axes (Oesterling et al. 1995). As regards the barrier against internal rotation (V_3), our value of 398.8 cm^{-1} is close to the older value of 402 cm^{-1} (Plummer et al. 1986).

3. DISCUSSION

With the spectroscopic constants of Table 3, we can predict the frequencies of many unmeasured lines including those outside of the measured frequency range. Predicted frequencies through 700 GHz with 1 σ uncertainties are listed in Tables 4 and 5 for the A and E torsional substates, respectively (only the first 20 rows of each table are found in the paper edition; for the complete versions, see the electronic edition). For transitions listed in both Table 1 or 2 and Table 4 or 5, astronomers should use the assigned and fitted frequency values in preference to the predicted values. The uncertainties listed in Tables 4 and 5 are to be treated cautiously. The transition frequencies and uncertainties are accompanied by quantum numbers, upper and lower state energies, and intensities. The constraints used to limit the number of predicted transition frequencies in Tables 4 and 5 are as follows: uncertainty ≤ 3.0 MHz, $J \leq 50$, frequency ≤ 700 GHz, $\mu^2 S \geq 0.10$, $E_{\rm lower} \leq 1000$ cm^{-1}. Nevertheless, there are over 12,000 predictions excluding those transitions already listed in Tables 1 and 2. Many of the transitions in Table 5 involving high K_a quantum number show c-type selection rules. An auxiliary list of predicted transition frequencies from 700 through 1500 GHz is available from the authors. The list consists of b-type and c-type transitions only; the stronger a-type transitions are not included because in this frequency range they involve higher J quantum numbers than we have calculated.

Since the energy difference between the lowest rotational levels of the $v_t = 0$ A and E torsional substates in methyl

TABLE 4

PREDICTED TRANSITION FREQUENCIES OF METHYL FORMATE IN THE GROUND A TORSIONAL SUBSTATE

J'	K_a'	K_c'	J''	K_a''	K_c''	Frequency (MHz)	Uncertainty (MHz)	E_u (cm^{-1})	E_l (cm^{-1})	$\mu^2 S$
20	10	11	21	9	12	1034.310	0.017	132.3	132.3	0.9
20	10	10	21	9	13	1036.245	0.017	132.3	132.3	0.9
30	9	21	30	9	22	1040.566	0.003	229.4	229.3	12.0
26	8	18	26	8	19	1137.767	0.003	174.4	174.4	11.1
14	5	9	14	5	10	1148.438	0.002	54.8	54.8	8.6
43	12	31	43	12	32	1159.588	0.005	457.3	457.2	13.5
22	7	15	22	7	16	1203.669	0.003	127.0	127.0	10.3
18	6	12	18	6	13	1216.798	0.002	87.1	87.1	9.4
40	19	22	41	18	23	1316.496	0.060	502.7	502.6	2.4
40	19	21	41	18	24	1316.498	0.060	502.7	502.6	2.4
39	11	28	39	11	29	1363.921	0.004	378.1	378.1	12.8
7	3	4	7	3	5	1517.701	0.003	15.7	15.6	6.2
35	10	25	35	10	26	1578.149	0.004	306.5	306.4	12.1
48	13	35	48	13	36	1583.740	0.012	564.0	564.0	13.4
1	1	0	1	1	1	1610.247	0.001	0.9	0.8	4.0
39	17	22	38	18	21	1630.815	0.042	453.3	453.3	2.2
39	17	23	38	18	20	1630.815	0.042	453.3	453.3	2.2
31	9	22	31	9	23	1792.087	0.005	242.3	242.3	11.3
3	2	1	4	1	4	1836.802	0.014	4.3	4.3	0.1
19	8	12	18	9	9	1876.939	0.018	107.6	107.5	0.8

NOTE.—Table 4 is published in its entirety in the electronic edition of The Astrophysical Journal. A portion is shown here for guidance regarding its form and content.

formate is miniscule (the E state $J = 0$ level lies 0.013 $cm^{-1} = 0.02$ K above its A counterpart), the energy separation need not be considered in computations of the rotational partition function for methyl formate. The A and E torsional substates do have different associated proton spin wave functions and are analogous to ortho-para states of other molecules. The nuclear spins compensate for the extra twofold degeneracy of the E torsional substates so that both the A and E substates can be regarded as having the same degree of torsional-nuclear spin degeneracy (Townes & Schawlow 1975), which can be neglected. Furthermore, since the internal rotor effects in methyl formate are small and the molecule is heavy, the classical approximation for the rotational partition function (Townes & Schawlow 1975) is valid for all temperatures down to 10 K. One must remember, however, to multiply the value obtained by a factor of 2, to account for the two torsional substates. Since the exact position of the excited torsional states is not yet determined, one can only estimate their effect on the overall partition function. We estimate that neglect of the excited torsional states underestimates the partition factor by a factor of a few at 300 K, so that in the warmer portions of

TABLE 5

PREDICTED TRANSITION FREQUENCIES OF METHYL FORMATE IN THE GROUND E TORSIONAL SUBSTATE

J'	K_a'	K_c'	J''	K_a''	K_c''	Frequency (MHz)	Uncertainty (MHz)	E_u (cm^{-1})	E_l (cm^{-1})	$\mu^2 S$
20	10	10	21	9	12	1025.910	0.019	132.3	132.3	0.9
47	13	34	47	13	35	1028.917	0.040	543.9	543.9	12.5
30	9	21	30	9	22	1038.592	0.003	229.4	229.3	12.0
26	8	18	26	8	19	1138.953	0.005	174.4	174.4	11.1
14	5	9	14	5	10	1172.199	0.009	54.8	54.8	8.2
10	4	6	9	5	5	1175.549	0.041	30.0	30.0	0.1
43	12	31	43	12	32	1195.435	0.023	457.3	457.2	12.7
22	7	15	22	7	16	1212.747	0.008	127.0	127.0	10.1
18	6	12	18	6	13	1234.230	0.009	87.1	87.1	9.1
40	19	21	41	18	23	1288.446	0.065	502.7	502.6	2.4
40	19	22	41	18	24	1326.662	0.062	502.7	502.6	2.4
39	11	28	39	11	29	1379.826	0.012	378.1	378.1	12.5
7	3	4	7	3	5	1528.771	0.006	15.7	15.7	6.1
35	10	25	35	10	26	1580.685	0.006	306.5	306.4	12.0
1	1	0	1	1	1	1610.900	0.001	0.9	0.9	4.0
48	13	35	48	13	36	1619.924	0.108	564.0	564.0	12.8
39	17	23	38	18	21	1620.303	0.045	453.3	453.3	2.2
39	17	22	38	18	20	1656.689	0.048	453.3	453.3	2.2
31	9	22	31	9	23	1788.942	0.005	242.3	242.3	11.3
3	2	1	4	1	4	1827.971	0.013	4.3	4.3	0.1

NOTE.—Table 5 is published in its entirety in the electronic edition of The Astrophysical Journal. A portion is shown here for guidance regarding its form and content.

hot cores, there may be more methyl formate than has been heretofore estimated.

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